

ISOTOPES ^3H , $\delta^2\text{H}$ AND $\delta^{18}\text{O}$ IN GROUNDWATERS FROM VOJVODINA REGION



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Content of the presentation



- The results of the survey of groundwater samples from Vojvodina region, Serbia.
- In this project, ^3H , $\delta^2\text{H}$ and $\delta^{18}\text{O}$ were analyzed.
- For understanding and interpretation of the results, geology and hydrology of the researched area was taken into consideration.
- This research was financed by Provincial Secretary for Science and Technological Development of AP Vojvodina under the one-year project:

“Investigation of the groundwater characteristics by electrolytic enrichment method”

The aim and importance of the study



- The subject of research are groundwater samples from Vojvodina region.
- It is estimated that underground waters provide around 70% of water needs in households and for industry in Serbia, and in Vojvodina region the groundwater is often the only source of water supply.
- According to the available statistical data and estimations of the quantity of used water for the purpose of public and individual supply for agricultural purposes, today in Serbia people use more than 500,000,000 m³ of groundwater.
- The total capacity of the existing groundwater sources in Serbia are around 678,000,000 m³ per year or 21.5 m³/s, from which 6.5 m³/s for Vojvodina and 15 m³/s for Central Serbia.
- Pannonia basin area includes Vojvodina region and has the compact aquifer artesian and sub-artesian character. This region is characterized by overexploitation and insufficient regeneration which causes the deficits in water supply.
- It is important to know the approximate age and origin of groundwater for better water resources planning and management.
- **This is the first time that the age and origin of groundwater samples from Vojvodina region were determined!**

Radioactive isotope of hydrogen– ^3H



- By measuring the activity concentration of radioactive isotope tritium, half-life (4500 ± 8) days, the groundwater's age could be estimated.
- ^3H is a low-energy (18.6 keV) beta emitter commonly used as a radiotracer in environmental research.
- Tritium acts like stable hydrogen atom and can be linked to the water molecules as a substitute to stable hydrogen atom.
- Tritium is directly incorporated into the water molecule (H^3HO), so it participates in the hydrological cycle and can be detected in groundwater.
- Tritium is present in the environment both as a natural (cosmic) and anthropogenic isotope.
- The presence of tritium in groundwater indicates recharge of aquifer by modern precipitation (i.e., recharge after 1952).
- Modern groundwater is renewable, as opposed to the older and fossil water, and in this sense it can be better utilized. On the other hand, modern groundwater is more vulnerable to contamination from the surface.
- Activity concentration of tritium can be measured both by proportional counter and liquid scintillation counter (LSC). LSC has better performances, especially for measuring tritium in natural waters.

^3H – groundwater age?

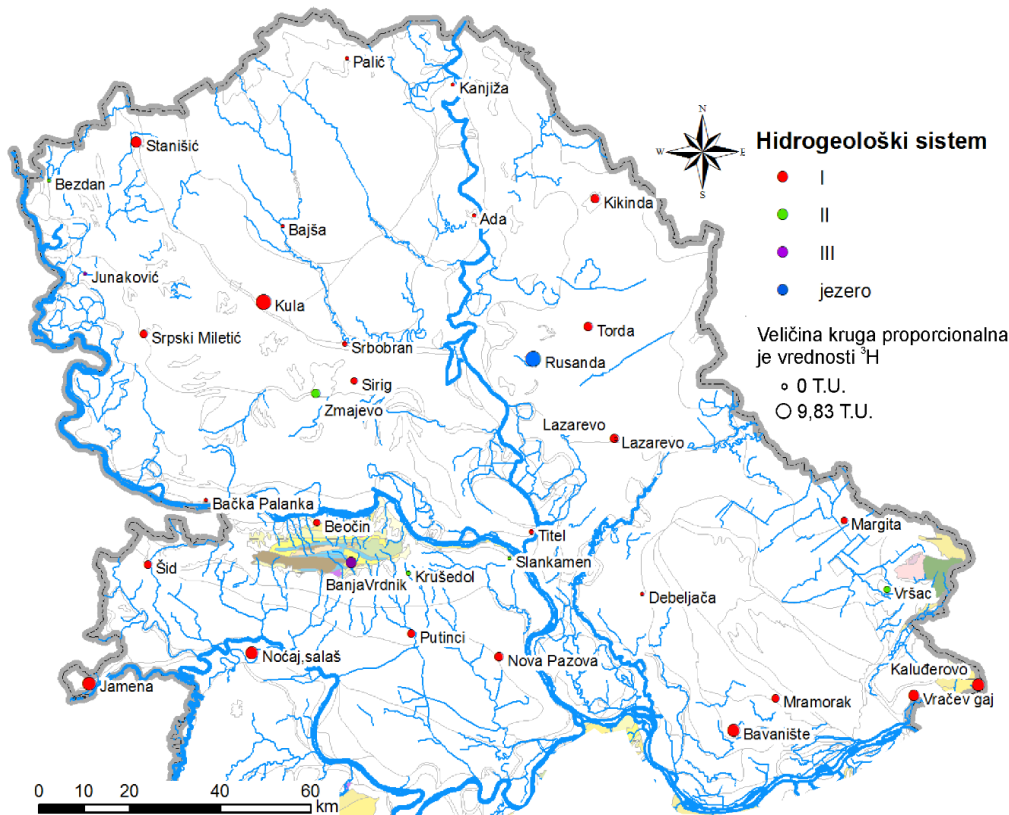


- By measuring of the activity concentration of ^3H we can estimate the age of analyzed groundwater.
- The existence of ^3H in groundwater leads to the conclusion that the hydrological system has recharged with waters younger than 63 years.
- The terminology **groundwater age** is critical because in this exact case we do not speak about the age of waters (in the sense of people aging), this terminology is used here to state the differences between groundwater that have been recharged naturally in the last 60 years from precipitations and the other ones that are source waters and don't have such fast flow and changing of water.
- The activity concentration of tritium is usually expressed in the tritium units (TU) - 1 TU is 0.118 Bq/l.
- According to the one possible classification (Motzer, 2007):
 - <0.8 TU means that water is sub-modern (older than 63 years; before 1952),
 - 0.8 - 4 TU shows that the mixing of modern and sub-modern waters is present,
 - 5 - 15 TU modern waters (<5 to 10 years),
 - 15 - 30 TU this waters were affected by the higher activity concentrations of tritium in the atmosphere during bomb testing and/or nuclear accidents,
 - >30 TU recharging of groundwater was between 1960 - 1970,
 - >50 TU recharging of groundwater was during 1960s.

Sampling



- The sampling locations were chosen with the aim of achieving a uniform spatial representation, so as sampling water from different hydrological systems. We analyzed 35 groundwater samples from dug wells, drilled wells and natural springs and one surface water sample from the lake.



Legend:

- Quaternary sediments;
- Pliocene (lake-swamp, clastic and pelitic formation);
- Miocene sediments;
- Gneiss and migmatite;
- Diorite to gabbro;
- Flysch of Fruška gora (sandstone, alevrolite and shale, conglomerate);
- Jurassic (serpentinite, peridotite, ophiolite melange);
- Triassic sediments (conglomerates, sandstones, alevrolites, shale);
- Gneiss and micaschist;
- Schist, metasandstone, quartzite, phyllite, marble)

Geology and hydrology of the examined area



- Four hydrological systems are distinguished in Vojvodina region (Aksin and Milosavljević, 1982):
 - **First hydrological system** is the most widespread in the region, with a number of water-bearing bed. The system provides a good porosity and permeability, and good recharge conditions. It is most important hydrological system for the water supply of the population. Thermal and thermo-mineral waters are located in it as well. This system comprises sediments from the surface to the basement of upper Pontian age (Pl₁). It is developed throughout Vojvodina region, except at Mt. Fruška Gora and Vršac Mountain area. Groundwater aquifer is made of sands and gravels of different size, while clays and marls are the isolator. In the shallowest parts of terrain, up to 60 m of depth, unconfined groundwater reservoir is present (sediments of Holocene). In the deeper Pliocene and Pleistocene sand/sandstone sediments, confined groundwater reservoir is present.
 - **Second hydrological system** is placed below the first one, and is composed of the sediments from Pontian and Pannonian age. Groundwaters are present in locally developed sandstones, but the majority of rocks are non permeable marls. This hydrogeological system represent hydraulic barrier between the first and third.
 - **Third hydrological system** is made of rocks of Miocene, Paleogene, Jurassic and Cretaceous period. Reservoir rocks are sandstones, conglomerates, limestone and breccia, and isolators are marls and shales. Majority of groundwater originates from the fractured Triassic limestone and dolomite.
 - **Fourth hydrological system** is developed in igneous, metamorphic and sedimentary rocks of Triassic period and Paleozoic era.

Aksin, V., Milosavljević, S. (1982) *Geotermalni potencijali SAP Vojvodine - istraživanje i korišćenje*. Novi Sad

Sample preparation and measurements

- **Sample preparation:** All 36 samples were prepared by electrolytic enrichment method at Ruđer Bošković Institute, Zagreb, Croatia.
- **Measurment:** Prepared samples were measured by ultra-low level Liquid Scintillation Counter Quantulus 1220, in both laboratories – Faculty of Sciences, Novi Sad, Serbia and Ruđer Bošković Institute, Zagreb, Croatia.



Elelctrolityc enrichment method



Liquid Scintilation Counter – Quantulus 1220, Perkin Elmer

Sample preparation

- The activity concentration of ^3H in groundwater samples is expected to be low, so the electrolytic enrichment is necessary.
- Electrolytic enrichment was done on the device that consist of 20 electrolytic cells, and from the 500 ml of water at the end we get (19 ± 1) ml of sample with enrichment factor of (22.5 ± 0.5) .
- MDA is around 0.5 TU.



Measurement – liquid scintillation counter

- 8 ml of enriched water is mixed with 12 ml of scintillation cocktail (in Zagreb UltimaGoldLLT is used, and in Novi Sad Optiphase HiSafe 3 is used).
- The measuring time of 90 minutes is usually enough for measuring of enriched samples, the measurement is usually done in few cycles.
- LSC Quantulus 1220 is a low level detector which has their own background reduction system around the chamber with the sample. It has passive and active shield.
- Passive shield is made from the lead, copper and cadmium, and active shield is based on mineral oil scintillators.



Stable isotope measurement

- Stable isotopes $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in all samples were measured in Geological Survey of Croatia, Zagreb, Croatia. The ratio of stable isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) is measured on the spectrometer Picarro L2130i, which uses Cavity Ring Down Spectrometry (CRDS) measuring technique. Results of this measurements are presented in [‰] relatively to standard V-SMOW.



Results – older waters, more than 60 years

In 3 groundwater samples (Kanjiža, Slankamen and Debeljača) the activity concentrations were 0.89 TU, 0.84 TU and 0.9 TU, which is slightly above Motzer's limit (0.8 TU). All three samples have very high mineralization, and two of them also a high temperature, which ensures that those waters are older, spent more time in between the surrounding rocks. Except this, water from Kanjiža is sampled from the dipper horizon (1008 to 1085 m), as well as sample from Bezdán in which low activity concentration of tritium is measured (<0.8 TU).

Water sample from Debeljača is taken from the same geological area as sample from Lazarevo, from deeper well (80 m).

Location	A [TU]
1. Ada	0.64 ± 0.09
2. Kanjiža	0.89 ± 0.12
3. Palić	0.72 ± 0.09
4. Slankamen	0.84 ± 0.10
5. Bezdán	<0.5
6. Prigrevica	<0.5
7. Debeljača	0.9 ± 0.4
8. Lazarevo, 80 m	<0.5
9. Bajsa – Bačka Topola	<0.5

Results– mixture of older and modern waters

- In 8 samples, activity concentrations of ^3H were between 0,9 and 4 TU and slightly above 4 TU, but less than 5 TU.
- All of this samples were taken from duged wells, so the obtained values indicate the mixing of older waters from deeper horizons and younger, modern waters (percipitations).

Location	A [TU]
1. Srbobran	2.1 ± 0.5
2. Bačka Palanka – Obrovac	1.36 ± 0.19
3. Titel	2.6 ± 0.6
4. Plandište – Margita	3.6 ± 0.5
5. Sirig	3.4 ± 0.4
6. Vršac	3.7 ± 0.5
7. Bavanište	1.3 ± 0.4
8. Beočin	4.0 ± 0.8

Results – modern waters



On the Vojvodina region there are mostly modern waters, less than 10 years.

Location	A [TU]	Location	A [TU]
1. Šid	4.8 ± 1.0	11. Nova Pazova	5.8 ± 1.0
2. Kikinda	6.0 ± 0.8	12. Torda	5.8 ± 1.0
3. Lazarevo, 40 m	5.5 ± 1.0	13. Zmajevio	5.4 ± 0.9
4. Mramorak	4.6 ± 0.7	14. Banja Vrdnik	6.7 ± 1.2
5. Bela Crkva - Kaluđerovo	7.0 ± 1.0	15. Srpski Miletic	4.3 ± 0.6
6. Bela Crkva – Vračev Gaj	6.4 ± 0.9	16. Stanišić	6.1 ± 0.8
7. Kula	9.7 ± 1.8	17. Bavanište	7.9 ± 1.2
8. Jamena	8.2 ± 1.6	18. Sremski Karlovci	7.5 ± 1.4
9. Noćaj, salaš	7.3 ± 1.4	19. Lake Rusanda	9.8 ± 1.5
10. Putinci – Ruma	4.6 ± 0.9		

Results – isotopes $\delta^2\text{H}$ and $\delta^{18}\text{O}$



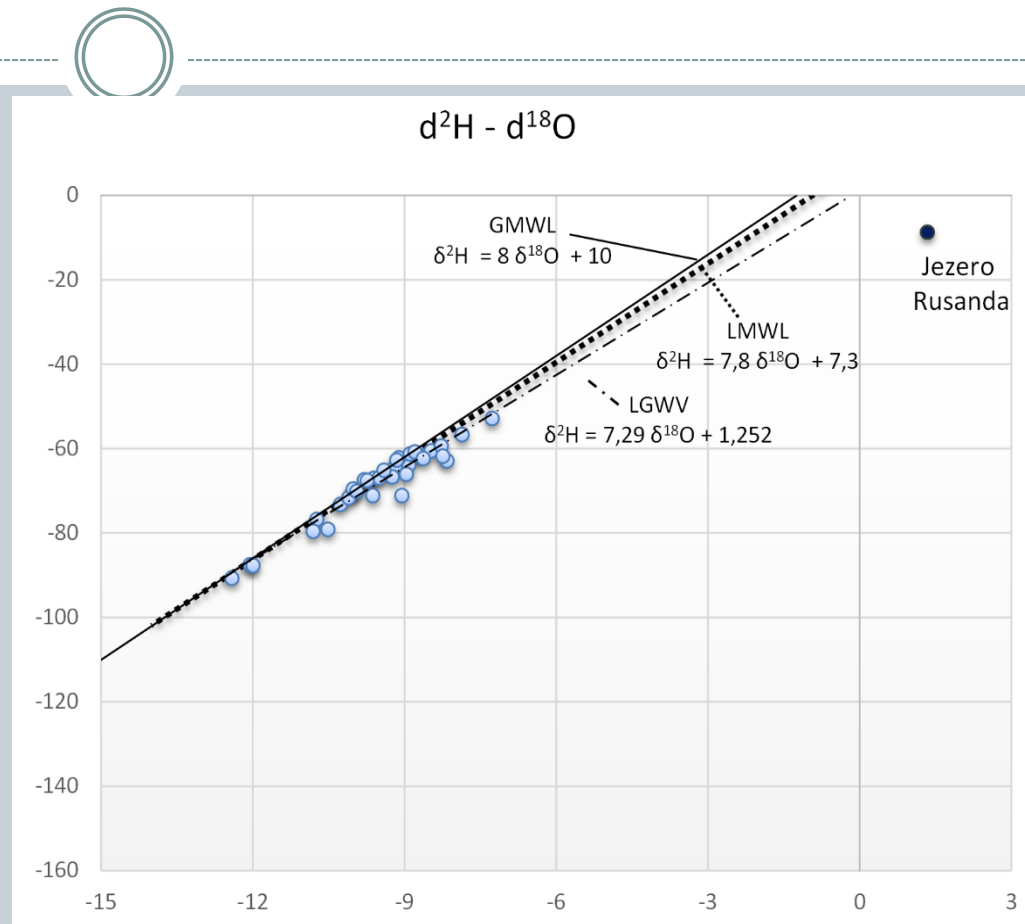
- Analysis of stable isotopes $\delta^2\text{H}$ and $\delta^{18}\text{O}$ were made in all samples of groundwater and in the sample from lake Rusanda.
- These isotopes are used in estimating the groundwater recharge of Vojvodina.
- The values of isotopes range from -7.3 to -12.4 ‰ for $\delta^{18}\text{O}$ and from -52.9 to -90.7 ‰ for $\delta^2\text{H}$, while value of lake Rusanda is 1.3 ‰ for $\delta^{18}\text{O}$ and 8.7 ‰ for $\delta^2\text{H}$.
- The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the groundwater in the wells were observed to be lighter (more negative) than in the lake, which were enriched with the heavy isotopes due to intensive evaporation losses in lake.

Results – isotopes $\delta^2\text{H}$ and $\delta^{18}\text{O}$

- Values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ lie along to global meteoric line which confirms that the analysed groundwater recharge from precipitation.
- Minor deviation of the groundwater isotopic data below the relevant meteoric line, indicate that the waters are ancient and that were recharged in a different climate regime.

according to the reference

Mazor E., 2007. Chemical and Isotopic Groundwater Hydrology, Marcel Dekkerinc



Content of $\delta^{18}\text{O}$ - $\delta^2\text{H}$ in groundwater and lake Rusanda
Legend: GMWL-Global meteoric water line (Craig, 1961);
LMWV - Meteoric water line of Belgrade (Globočanin et al, 2007);
LGWV – Groundwater line of lake Rusanda

Conclusion



- Majority of groundwaters are captured from the first hydrological system. These groundwaters originate from the youngest sediments, so the aim of this project was (based on the value of tritium) to define whether the youngest water are formed in the youngest sediments.
- According to the obtained results of measurement, the estimation of the groundwater age and origin of the examined water samples was done.
- Between 36 measured water samples (35 groundwater and 1 surface water) maximum activity concentration of ^3H was **9.8 TU**, and only in 2 groundwater samples activity concentrations of ^3H were below MDA.

Conclusion



- Beside ^3H in all water samples, isotopes $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were measured, which gives additional value to the interpretation of the results.
- Problems on terrain:
 - there is not enough reliable data about wells (depth) so the recognition of the exact hydrological system was difficult.
 - For dugged wells there are no litological profiles of the wells..
- According to the obtained results we can conclude that there is no regularity of groundwater age and the hydrological sytem that it belongs to.
- I hydrological system consists of the younger sediments and there are some older groundwater in this system. In the II and III hydrological systems we have samples from deeper groundwater and those waters are younger according to the analysis. This could be explained by water circulation, which ensures that water goes to deeper horizons.
- Samples from Lazarevo and Debeljača gave also interesting results, those waters are taken from depth of 80 m from the I hydrological system , and according to the activity concentration of tritium those waters belongs to older waters. This means that in this geological area waters stay longer.
- **Waters from one hydrological system could be of different age and origin!** It is therefore important for the analysis to include as many as possible locations and to take into consideration the additional parameters which may be a subject for some future research ...

Thank you for your attention!

